Supporting Information for

Understanding the Role of Bulky Side Chains on Polymorphism of BTBT-based Organic Semiconductors

Hyunjoong Chung[1], Shanwen Chen[1], Bijal Patel[1], Guillaume Garbay[2], Yves H. Geerts[2], Ying Diao[1]

[1]*Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana−Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801, United States.*
[2]*Laboratoire de Chimie des Polymères Faculté des Sciences, Université Libre de Bruxelles (ULB), CP206/1, Boulevard du Triomphe, 1050 Brussels, Belgium*

*email: yingdiao@illinois.edu

Contents

Supplementary Figures

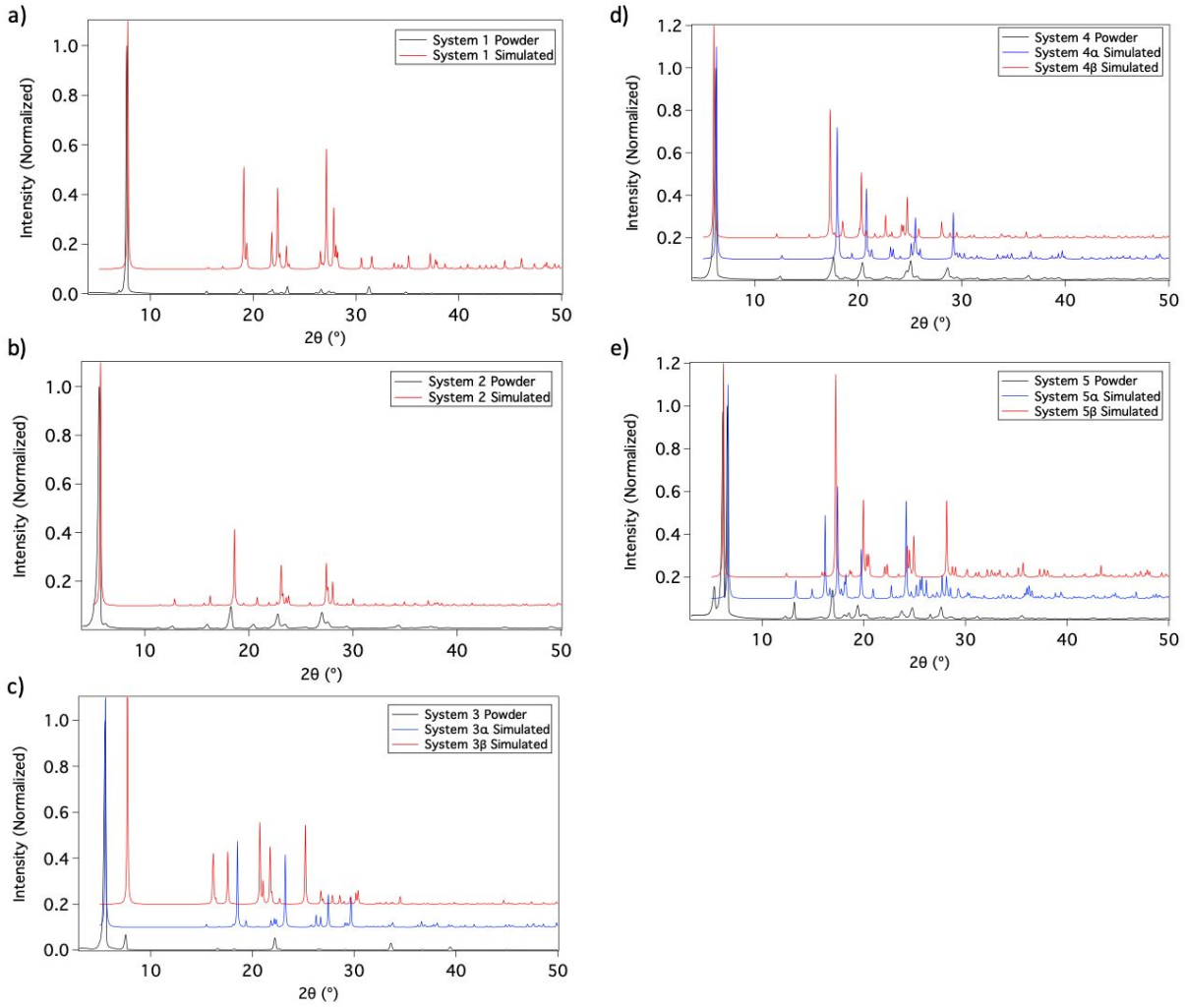

Figure S1. Powder X-ray diffraction of all systems with overlay of simulated spectra. Powder of system 3 contains both α and β polymorph, 4 contains α polymorph, and 5 contains α, β, and possibly even a third unknown polymorph.

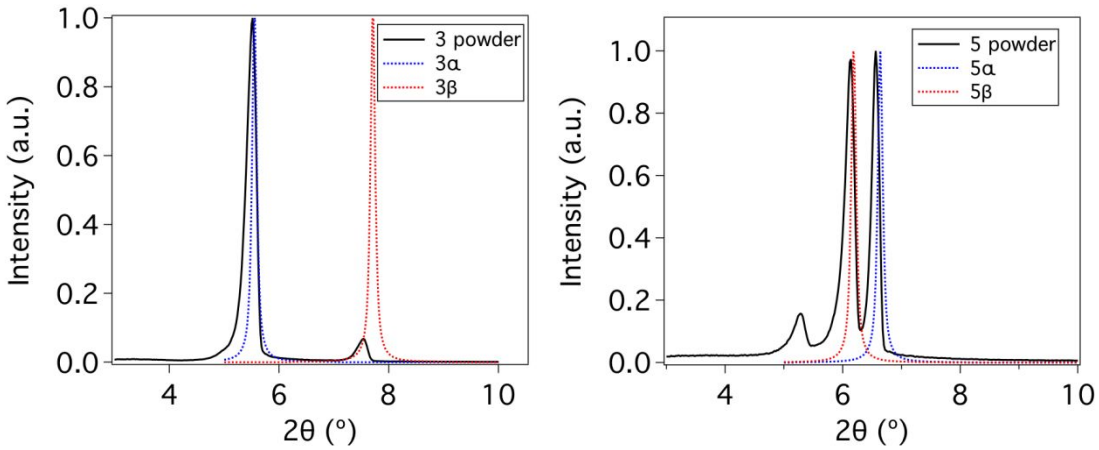

Figure S2. Powder X-ray diffraction (pXRD) data of system 3 and 5. Both α and β forms were present in 3 and 5, and interestingly, in 5, a third polymorph was also present. We could not access this form as single crystals and thus could not obtain the full crystal structure.

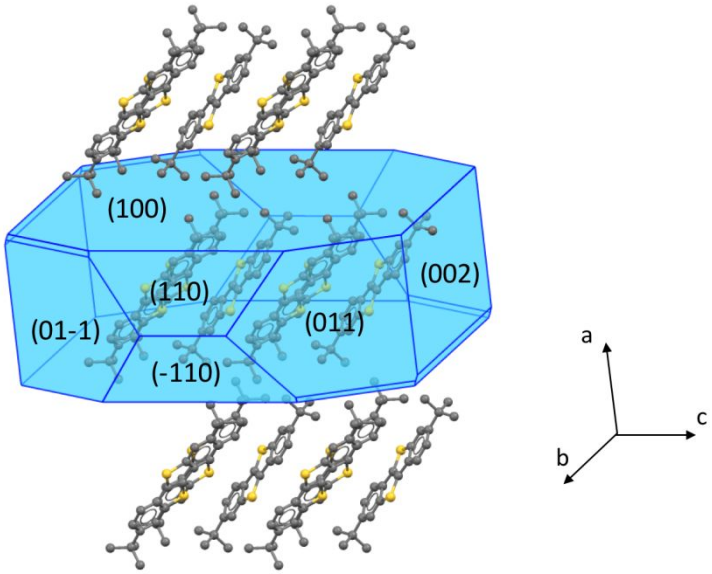

Figure S3. A representative Bravais-Friedel-Donnay-Harker (BFDH) morphology calculations of system 4. Each layer stacks out-of-plane of the crystal, and this is consistently observed in all five systems. Major (hkl) planes noted on figure. Hydrogen atoms are omitted for clarity.

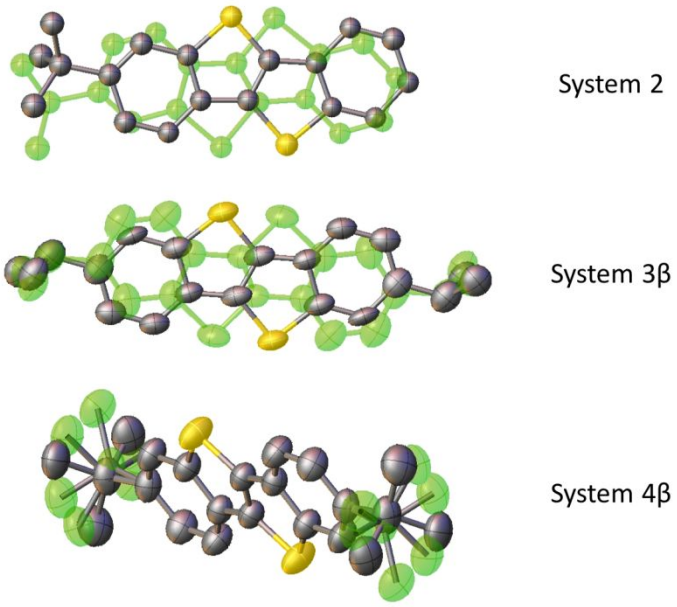

Figure S4. Ellipsoid representation of disorders in system 2, 3β, and 4β from OLEX2[4]. Green molecules indicate disordered parts. Static disorder exists in system 2 and 3β, 180° flipped from original molecule. System 4β shows dynamic disorder specifically in the side-chains.

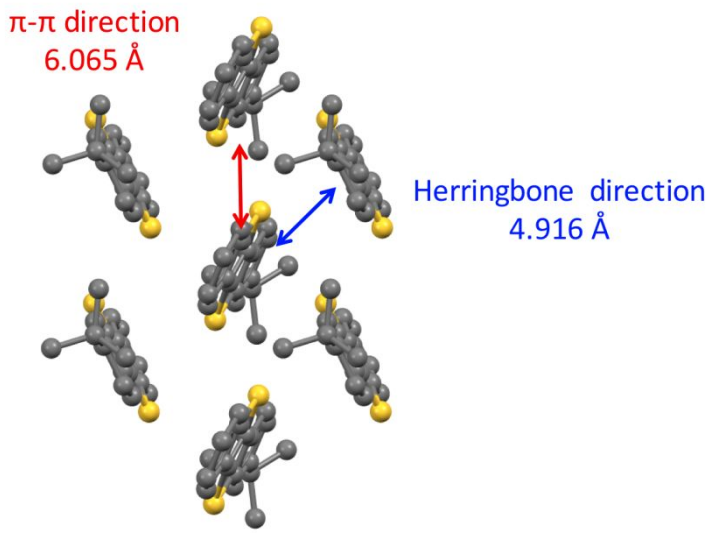

Figure S5. Display of the herringbone and π-π pair in **2**. The single side-chains are on opposite ends of the core in the herringbone pair and on the same side in the π-π pair. The center - center distance from the BTBT core are shown.

Supplementary Tables

System	1	2		3α			3β	4	5α			5β			
Solvent	tetralin	DMF	DMSO	decane	Tetralin	DMF	N/A	Tetralin	Tetralin	Tetralin	Ethyl acetate	Tetralin	Toluene	Acetone	CF
c ($mg\ mL^{-1}$)	10	15	5	8~15	10	10	N/A	10	10	3	2	6	5	1	5
Method	Dropcast on Si or well plates	Dropcast on Si	Dropcast on Si or well plates	Dropcast on Si, OTS-Si, and well plates	Dropcast on well plates	Dropcast on well plates	Sub.	Dropcast Slow evap.	Dropcast on well plates	Slow evap.	Slow evap. using α crystal seed	Dropcast on well plates	Slow evap.		

Green columns: Single crystals used for SCXRD
c: concentration DMF: dimethylformamide DMSO: dimethyl sulfoxide CF: chloroform Sub.: sublimation evap: evaporation

Table S1. Single crystal fabrication conditions for all BTBT systems.

System	P (°)	R (°)	d (Å)	d_p (Å)	d_r (Å)
1	29.08	61.44	2.79	1.55	5.13
2	21.95	64.58	2.60	1.05	5.48
3α	21.08	64.39	2.65	1.02	5.53
3β	42.48	61.24	2.90	2.66	5.28
4α	14.44	62.62	2.78	0.71	5.36
4β	7.33	61.60	2.99	0.38	5.52
5α	68.78	65.12	2.57	6.62	5.54
5β	13.86	61.67	2.98	0.73	5.52

Table S2. Pitch and roll angles and distances for the BTBT systems. P and R indicate pitch and roll angles, d indicates the π-π distance, d_p and d_r indicates pitch and roll distances[5].

	1	2	3α	3β	4α	4β	5α	5β
Density (g cm^{-1})	1.51	1.37	1.35	1.28	1.31	1.22	1.29	1.28
% change from 1	-	-9.3	-10.6	-15.2	-13.2	-19.2	-14.6	-15.2
Herringbone distance (Å)	4.94	4.916 4.886	5.122	6.651	6.081	6.094	6.316 6.174	6.400
% change from 2	0.5	-	4.2	35.3	23.7	24.0	28.5	30.2

Table S3. Calculated density and herringbone distance in all BTBT systems.

System	Atom 1	Atom 2	Distance (Å)	Distance - vdw (Å)
1	S	S	3.554	-0.046
	C	S	3.461	-0.039
	C	S	3.366	-0.134
	C	H	2.797	-0.103
	C	H	0.814	-0.086
	C	S	3.432	-0.068
2	S	S	3.565	-0.035
	C	S	3.466	-0.034
	C	S	3.398	-0.102
	C	S	3.495	-0.005
	C	S	3.432	-0.068
	C	S	3.438	-0.062
3α	C	S	3.427	-0.073
	C	S	3.476	-0.024
3β	S	S	3.335	-0.265
	C	H	2.885	-0.015
4α	C	H	2.898	-0.002
5α	S	H	2.927	-0.073
5β	C	H	2.867	-0.033

Table S4. List of short contacts and their corresponding atoms, distances between atoms, and distances subtracted from the van der Waals radii (abbreviated in the table as vdw).

Supplementary Movies

Movie S1. System 1 under CPOM upon heating. No polymorphic transition observed, and crystal sublimed.

Movie S2. System 2 under CPOM upon heating. No polymorphic transition observed, and crystal sublimed.

Movie S3. System 3 under CPOM upon heating. Polymorphic transition observed.

Movie S4. System 4 under CPOM upon heating. Polymorphic transition observed.

Movie S5. System 5 under CPOM upon heating. Polymorphic transition observed.

References

1. Schweicher, G.; Lemaur, V.; Niebel, C.; Ruzie, C.; Diao, Y.; Goto, O.; Lee, W. Y.; Kim, Y.; Arlin, J. B.; Karpinska, J.; Kennedy, A. R.; Parkin, S. R.; Olivier, Y.; Mannsfeld, S. C. B.; Cornil, J.; Geerts, Y. H.; Bao, Z. N., Bulky End-Capped [1]Benzothieno[3,2-b]benzothiophenes: Reaching High-Mobility Organic Semiconductors by Fine Tuning of the Crystalline Solid-State Order. *Adv. Mater.* **2015,** *27*, 3066-3072.
2. Niebel, C.; Kim, Y.; Ruzié, C.; Karpinska, J.; Chattopadhyay, B.; Schweicher, G.; Richard, A.; Lemaur, V.; Olivier, Y.; Cornil, J.; Kennedy, A. R.; Diao, Y.; Lee, W.-Y.; Mannsfeld, S.; Bao, Z.; Geerts, Y. H., Thienoacene dimers based on the thieno[3,2-b]thiophene moiety: synthesis, characterization and electronic properties. *J. Mater. Chem. C* **2015,** *3*, 674-685.
3. Chung, H.; Dudenko, D.; Zhang, F. J.; D'Avino, G.; Ruzie, C.; Richard, A.; Schweicher, G.; Cornil, J.; Beljonne, D.; Geerts, Y.; Diao, Y., Rotator side chains trigger cooperative transition for shape and function memory effect in organic semiconductors. *Nat. Commun.* **2018,** *9*.
4. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** *42*, 339-341.
5. Curtis, M. David; Cao, Jie; Kampf, Jeff W. Solid-State Packing of Conjugated Oligomers: From π-Stacks to the Herringbone Structure. *J. Am. Chem. Soc.* **2004**, 126, 13, 4318-4328.